

# Chapter 2

## Photo-Induced Demulsification

Yutaka Takahashi and Yukishige Kondo

**Abstract** Demulsification is an aggressive phase-separation phenomenon of stable emulsions. Several studies have examined demulsification by chemical reactions using external stimuli, such as temperature variation, pH variation, and light irradiation. This study focused on the interfacial and emulsification properties of light-responsive surfactants because the use of light as an external stimulus is relatively simple. This chapter presents an overview of the photo-induced demulsification of emulsions prepared using light-responsive surfactants containing an azobenzene skeleton. Stable emulsions are obtained when mixtures of *n*-octane and aqueous solutions of azobenzene-containing surfactants are homogenized. Ultraviolet irradiation of the stable emulsions induces complete phase separation of the octane and aqueous surfactant solution phases. The phase separation, i.e., demulsification, results from a change in the interfacial properties, such as occupied areas per molecule and interfacial tension, of the light-responsive surfactants at the oil/water interface.

**Keywords** Photoresponsive surfactant • Azobenzene • Demulsification

### 2.1 Introduction

Photoresponsive surfactants exhibit interfacial properties that can be controlled by light irradiation at specific wavelengths [1–3]. Azobenzene, diarylethene, and spiropyran are well-known photoresponsive compounds that are converted reversibly between two isomers by a particular wavelength of light [4–7]. Several studies have examined ways of controlling the interfacial properties of photoresponsive surfactants containing an azobenzene [8–12]. The *trans* and *cis* isomers of azobenzene derivatives can be switched reversibly using a particular wavelength of

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light; the *trans* isomer is converted to the *cis* by ultraviolet (UV) light, and visible light irradiation converts the *cis* isomer to the *trans* isomer [7, 13].

Emulsions are metastable systems consisting of two immiscible liquids, such as water and oil. Surfactants have generally been used to stabilize emulsions. Therefore, the interfacial properties of the surfactants at the oil/water interface are important for the stability of emulsions. On the other hand, demulsification involves the breaking of stable emulsions into separate oil and water phases. The phenomenon is used as “emulsion liquid membrane extraction” [14], which is a technique to extract harmful substances from aqueous waste fluids. Thus far, demulsification has been carried out by adding demulsifiers to stable emulsions and applying some form of physical energy [15–18]. Recent studies have reported that the properties of emulsions containing stimuli-responsive materials can be controlled by external stimuli, such as pH variation and light irradiation. The stability of emulsions prepared using pH-responsive polymers changed drastically on varying the pH using acids or bases [19–26]. In some cases, however, the addition of acids or bases to emulsions is undesirable because the resulting emulsions are contaminated. In contrast, Eastoe et al. showed that UV irradiation induced the destabilization of the microemulsions containing a photodestructible surfactant and sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and reported their studies of photosensitive microemulsion [27–29]. They also demonstrated the photoinduced phase separation of single-phase microemulsions consisting of decane and aqueous solution of a photoresponsive surfactant and AOT mixtures by UV light irradiation [30]. In addition, Perrin et al. reported control of the emulsion types by UV and visible light irradiation [31]. Emulsions consisting of *n*-dodecane, water, sodium nitrate, nonionic surfactant, and amphiphilic photoresponsive polymers containing azobenzene groups were converted from the oil-in-water (O/W) type to the water-in-oil (W/O) type by UV light irradiation [32, 33].

This chapter provides an overview of two systems of photo-induced demulsification that were reported recently. One is the photo-induced demulsification of stable O/W-type emulsions prepared using a photoresponsive gemini surfactant with an azobenzene as a spacer [34], while the other system involves the photo-induced demulsification of stable emulsions prepared using mixtures of anionic and cationic surfactants [35].

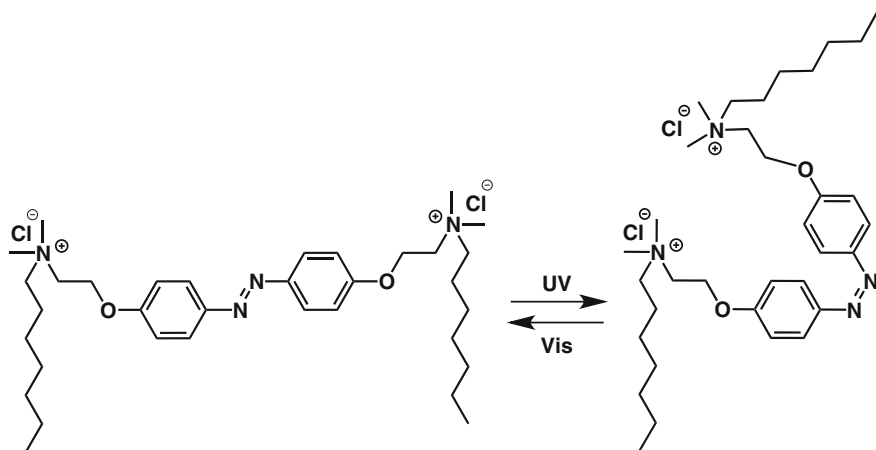
## 2.2 Demulsification of Photoresponsive Emulsions Using a Photoresponsive Gemini Surfactant

A few studies of gemini surfactants containing photoresponsive groups as a spacer have been reported. Shimomura et al. succeeded in inducing an orientational change in a gemini surfactant with a diarylethene group at the air/water interface by UV irradiation [36]. Oda et al. reported the formation and disruption of vesicles formed from photoresponsive gemini surfactants containing an azobenzene group by

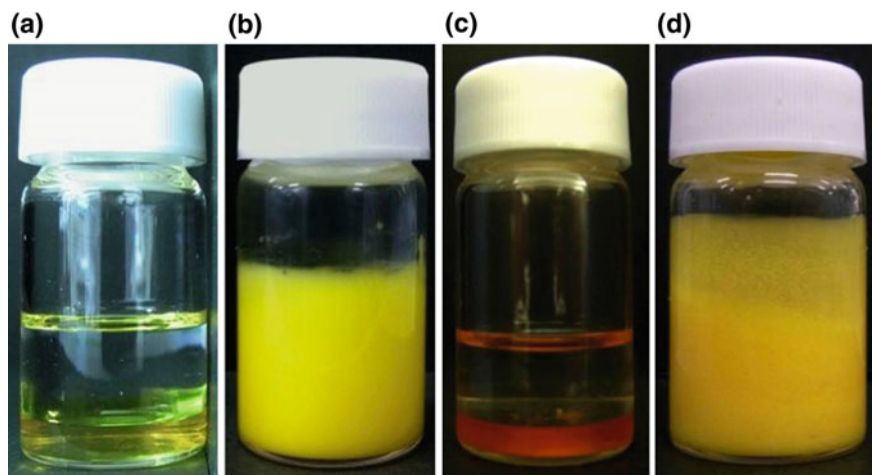
irradiation with UV and visible light [37, 38]. This chapter focuses on the photo-induced changes in the interfacial and emulsion properties of a photoresponsive gemini surfactant ( $C_7$ -azo- $C_7$ ; Fig. 2.1) at the oil/water interface [34].

Stable emulsions were obtained from mixtures of *n*-octane and aqueous *trans*  $C_7$ -azo- $C_7$  solutions at specific weight fraction and surfactant concentration. Emulsions consisting mixtures of *n*-octane and 10 mM of aqueous *trans*  $C_7$ -azo- $C_7$  solution (weight fraction of aqueous *trans*  $C_7$ -azo- $C_7$  solution ( $f_w$ ): 0.3) exhibited no phase separation over 1 week after preparation (Fig. 2.2b). When the fluorescent probes were added to the stable emulsions, fluorescence microscopy showed that the emulsions were the O/W type. As shown in Fig. 2.2c, the UV irradiation of stable O/W-type emulsions consisting of octane/10 mM of aqueous *trans*  $C_7$ -azo- $C_7$  solution ( $f_w$ : 0.3) for 6 h led to complete phase separation, i.e., demulsification. The *trans*  $C_7$ -azo- $C_7$  molecules in the emulsions were converted to the *cis* isomer by UV light irradiation. No phase separation was observed when stable O/W-type emulsions were stored for 6 h in the absence of UV irradiation in a dark room. Optical microscopy under UV light irradiation revealed the coalescence of octane droplets in the stable O/W-type emulsion. In contrast, 10 mM of aqueous *cis*  $C_7$ -azo- $C_7$  solutions were prepared by UV irradiation of the aqueous solutions of the *trans* isomer before homogenization. The emulsions showed no phase separation by the homogenization of mixtures consisting of *n*-octane and the aqueous *cis*  $C_7$ -azo- $C_7$  solution (Fig. 2.2d). No change in the stability of the emulsion was observed after irradiation with visible light. These results suggest that photo-induced demulsification occurs via a photoisomerization process from the *trans* to *cis* isomers in emulsions.

The photo-induced demulsification of stable O/W-type emulsions consisting mixtures of *n*-octane and 10 mM of aqueous *trans*  $C_7$ -azo- $C_7$  solution is discussed

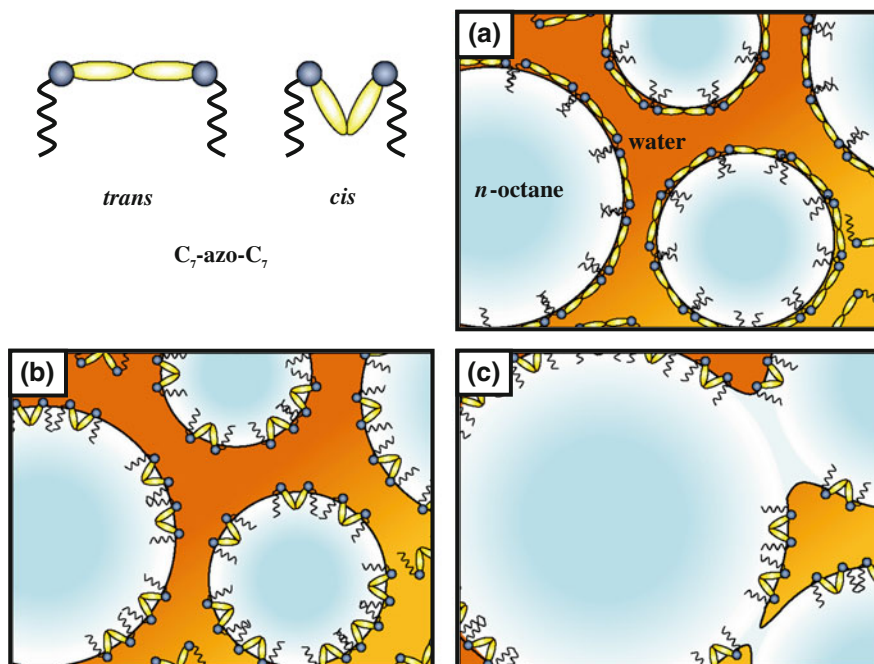


**Fig. 2.1** Chemical structure of the photoresponsive surfactant,  $C_7$ -azo- $C_7$ . The *trans* and *cis* isomers are shown. Reprinted with the permission from Ref. [34]. Copyright 2013 American Chemical Society



**Fig. 2.2** Photographs of **a** a mixture of *n*-octane and 10 mM of aqueous *trans* C<sub>7</sub>-azo-C<sub>7</sub> solution (*f<sub>w</sub>*: 0.3) before homogenization and **b** a stable emulsion obtained by homogenization. **c** Photo-induced demulsification of the emulsion shown in **(b)** by UV light irradiation on macroscopic scale. **d** An emulsion consisting of *n*-octane and the aqueous *cis* isomer of C<sub>7</sub>-azo-C<sub>7</sub> solution (no phase separation). Reprinted with the permission from Ref. [34]. Copyright 2013 American Chemical Society

from the results of the interfacial tensions measurements. An *n*-octane/aqueous C<sub>7</sub>-azo-C<sub>7</sub> solution of *trans* or *cis* isomers showed similar interfacial tension at a surfactant concentration of 10 mM. The occupied areas per molecule for *trans* and *cis* C<sub>7</sub>-azo-C<sub>7</sub> at the octane/water interface were estimated to be 3.2 and 1.6 nm<sup>2</sup>, respectively, from the Gibbs's adsorption isotherm and the slopes of the interfacial tension versus the surfactant concentration. Therefore, photoisomerization from the *trans* to *cis* isomer of C<sub>7</sub>-azo-C<sub>7</sub> molecule at the octane/water interface induced a decrease in the occupied areas per molecule at the interface. In addition, dynamic interfacial tension between octane and 10 mM of aqueous C<sub>7</sub>-azo-C<sub>7</sub> solutions with UV light irradiation was measured. When the octane/water interface-adsorbed *trans* C<sub>7</sub>-azo-C<sub>7</sub> molecules were exposed to UV light, the interfacial tension increased abruptly and then decreased gradually with increasing UV irradiation time. The value reached an equilibrated interfacial tension of *cis* C<sub>7</sub>-azo-C<sub>7</sub>. The abrupt increase in the dynamic interfacial tension with UV irradiation indicated an increase in the Gibbs free energy at the interface. This resulted from a reduction of the occupied areas per C<sub>7</sub>-azo-C<sub>7</sub> molecule at the octane/water interface with *trans*–*cis* photoisomerization, followed by the temporal and partial exposure (direct contact) of octane and water phases at the interface, contributing to an increase in the interfacial tension. From these results of the equilibrated and dynamic interfacial tension measurements, the authors suggested the following mechanism for the photo-induced demulsification of stable O/W-type emulsions prepared using C<sub>7</sub>-azo-C<sub>7</sub>. As shown in Fig. 2.3a, the C<sub>7</sub>-azo-C<sub>7</sub> molecules of the *trans* isomer were



**Fig. 2.3** Possible mechanism of the photo-induced demulsification of stable O/W-type emulsions prepared using  $C_7$ -azo- $C_7$ . **a** *trans*  $C_7$ -azo- $C_7$  molecules were adsorbed on the entire interface of *n*-octane and aqueous surfactant solution in the stable emulsions. **b** UV irradiation led to partial direct contact between the water and *n*-octane phases. **c** Exposure of the *n*-octane/water interface induced the coalescence of *n*-octane droplets in the emulsions. Finally, the *n*-octane and water phases were fully separated on a macroscopic scale. Reprinted with the permission from Ref. [34]. Copyright 2013 American Chemical Society

adsorbed on the entire interface between octane and the aqueous surfactant solution in the stable emulsions. UV irradiation induced a decrease in molecular area with photoisomerization from the *trans* to *cis* isomer and a temporal increase in interfacial tension between octane and the aqueous surfactant solution. This suggests that octane and water phases were contacted directly by the reduction of the azobenzene group in the  $C_7$ -azo- $C_7$  molecule at the octane/water interface (Fig. 2.3b). Exposure of octane/water interface led to the coalescence of octane droplets in the O/W-type emulsions to reduce the interfacial Gibbs free energy, followed by complete phase separation, i.e., demulsification (Fig. 2.3c).

Additional experiments were performed to confirm the mechanism of photo-induced demulsification described above. No phase separation was observed when a stable emulsion consisting of octane and a 10 mM aqueous solution of a gemini surfactant containing no azobenzene (1,2-bis(dodecyldimethylammonium) ethane dibromide) was exposed to UV light for 6 h. In addition, the emulsion remained the same after a stable emulsion consisting of octane containing a 10 mM

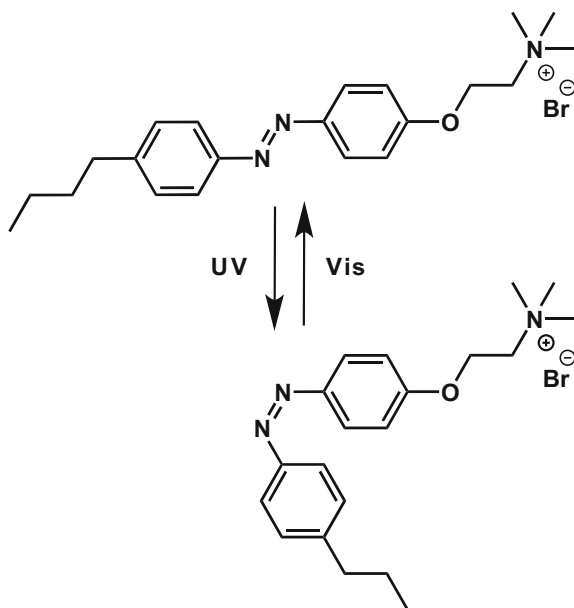
azobenzene and a 20 mM aqueous sodium dodecyl sulfate (SDS) solution was irradiated with UV light for 6 h. Therefore, the azobenzene group of a spacer in  $C_7$ -azo- $C_7$  molecule plays an important role in photo-induced demulsification.

In summary, stable O/W-type emulsions were obtained from *n*-octane and aqueous *trans*  $C_7$ -azo- $C_7$  solutions. UV irradiation of the stable emulsions promoted photo-isomerization from the *trans* to *cis* isomer and induced demulsification based on the coalescence of the octane droplets. The photo-induced demulsification resulted in a decrease in the molecular area of  $C_7$ -azo- $C_7$  at the oil/water interface.

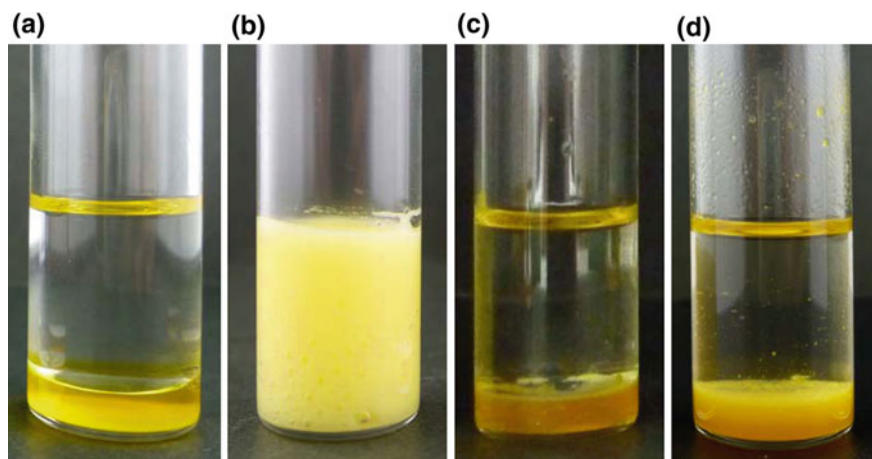
## 2.3 Demulsification of Photoresponsive Emulsions Using a Photoresponsive Catanionic Surfactant

As described above, it took 6 h to demulsify the stable emulsions prepared using  $C_7$ -azo- $C_7$  on a macroscopic scale. This does not appear to be useful in practical applications. Interfacial tension is one of important parameters controlling the stability of emulsions. Here, this section describes the photo-induced, demulsification-triggered increase in interfacial tension between *n*-octane and an aqueous solution containing an anionic surfactant (sodium dodecylsulfate, SDS) and a photoresponsive cationic surfactant (2-(4-(4-butylphenyl)diazenylphenoxy) ethyltrimethylammonium bromide, C4AzoTAB; Fig. 2.4) with UV irradiation [35]. In addition, the photo-induced demulsification rates were also investigated.

The emulsions were prepared by homogenizing mixtures of *n*-octane and an aqueous SDS/*trans*-C4AzoTAB solution (weight fraction of aqueous mixed-surfactant solution ( $f_w$ ): 0.2) at 25 °C. Stable O/W-type emulsions that exhibited no phase separation over 1 week after the preparation were obtained in the regions of the specific total surfactant concentrations ( $>5$  mM) and molar ratios ( $X_{SDS}$ ) of SDS in an aqueous SDS/C4AzoTAB solution ( $0 \leq X_{SDS} \leq 0.31$ ,  $0.7 \leq X_{SDS} \leq 1$ ). When stable O/W-type emulsions consisting of octane and 10 mM of aqueous SDS/C4AzoTAB solution with  $X_{SDS} = 0.1$  ( $f_w$ : 0.2) were irradiated with UV light, these octane and aqueous surfactant solution phases were separated gradually from the emulsions. As shown in Fig. 2.5c, the stable emulsions were demulsified by UV irradiation for 90 min, which was four times more rapid than the photo-induced demulsification of the stable emulsions prepared using  $C_7$ -azo- $C_7$  (6 h). UV irradiation caused the *cis* isomerization of *trans*-C4AzoTAB in the emulsions because the color of the aqueous SDS/C4AzoTAB solutions after UV irradiation for 90 min changed from yellow to reddish, corresponding to the *cis* isomer (Fig. 2.5). In addition, emulsions were obtained when mixtures of octane and a 10 mM aqueous SDS/*cis*-C4AzoTAB solution  $X_{SDS} = 0.1$  and  $f_w = 0.2$  in the photostationary state of the *cis* isomer were homogenized (Fig. 2.5d). Therefore, the UV irradiation of stable O/W-type emulsions induced the *cis* photo-isomerization of *trans*-C4AzoTAB molecules in the emulsions, leading to photo-induced demulsification. No phase separation was observed when stable



**Fig. 2.4** Chemical structure of the *trans* and *cis* isomers of a photoresponsive surfactant, 2-(4-(4-butylphenyl)diazenylphenoxy)ethyltrimethylammonium bromide (C4AzoTAB). Reprinted with the permission from Ref. [35]. Copyright 2016 American Chemical Society



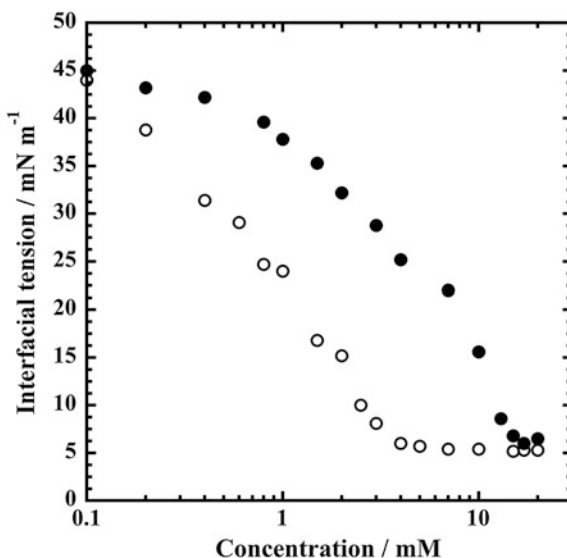
**Fig. 2.5** Photographs of a mixture consisting of *n*-octane and a 10 mM aqueous SDS/*trans*-C4AzoTAB solution with  $X_{\text{SDS}} = 0.1$  ( $f_w: 0.2$ ) at 25 °C **a** before homogenization and **b** a stable emulsion obtained by homogenization. **c** Photo-induced demulsification of the emulsion shown in **(b)** by UV irradiation on the macroscopic scale. **d** The mixture of octane and aqueous SDS/*cis*-C4AzoTAB solution in the photostationary state of the *cis* isomer was homogenized. No emulsion was obtained. Reprinted with the permission from Ref. [35]. Copyright 2016 American Chemical Society



emulsions obtained from octane and aqueous C4AzoTAB solution without SDS were irradiated with UV light. SDS in aqueous SDS/C4AzoTAB solutions plays an important role in photo-induced demulsification.

The authors examined possible mechanisms for the photo-induced demulsification of stable O/W-type emulsions prepared using SDS/C4AzoTAB mixtures. The number distributions of the diameter of octane droplets in the O/W-type emulsions consisting of octane and a 10 mM aqueous SDS/C4AzoTAB solution with  $X_{\text{SDS}} = 0.1$  ( $f_w$ : 0.2) exposed to UV light irradiation were estimated by observing the oil droplets through optical microscopy. The number-averaged diameter before UV light irradiation was  $14.6 \pm 9.2 \mu\text{m}$ . A change in the number distributions of the diameter of the octane droplets in the O/W-type emulsions with UV irradiation and optical microscopy observation under UV irradiation indicated that UV irradiation led to the coalescence of small octane droplets to larger ones in the emulsions, i.e., demulsification. Therefore, the photo-induced demulsification of stable emulsions prepared using SDS/C4AzoTAB mixtures resulted from Ostwald ripening. Equilibrated interfacial tension measurements indicated that the interfacial tension between *n*-octane and aqueous SDS/C4AzoTAB solutions with  $X_{\text{SDS}} = 0.1$  for both *trans* and *cis* isomers decreased with increasing surfactant concentration and reached constant values at specific concentrations (Fig. 2.6). However, the interfacial tension of the *cis* isomer was higher than that of the *trans* isomer over the range, 0.1–15 mM. In other words, UV irradiation induced increases in the interfacial tensions at specific surfactant concentrations. The authors also suggested the following mechanism for the photo-induced demulsification of stable O/W-type emulsions prepared from SDS/C4AzoTAB mixtures. SDS and *trans*-C4AzoTAB molecules were absorbed onto the entire octane/aqueous surfactant solution

**Fig. 2.6** Relationship between the interfacial tensions between *n*-octane and aqueous SDS/C4AzoTAB solution and the mixed-surfactant concentrations. Open circles *trans* isomer. Filled circles *cis* isomer. Reprinted with the permission from Ref. [35]. Copyright 2016 American Chemical Society

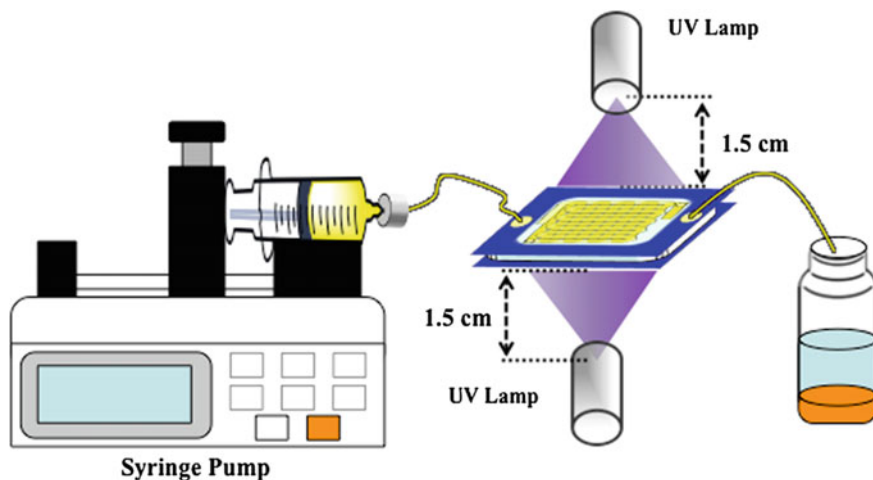




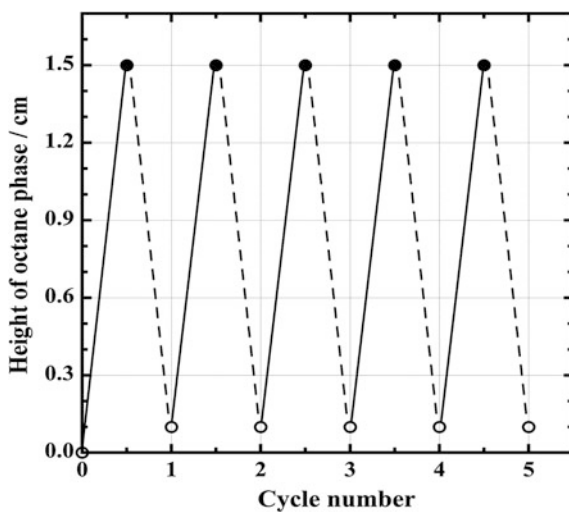
interfaces in the stable emulsions. UV irradiation led to *trans*–*cis* photoisomerization and an increase in interfacial tension at the octane/aqueous surfactant solution interface. The increase in interfacial tension with *trans*–*cis* photoisomerization caused the coalescence of smaller octane droplets to larger ones (Ostwald ripening) in O/W-type emulsions to reduce the interfacial area of the emulsions. Moreover, Ostwald ripening progresses with *trans*–*cis* photoisomerization until the octane and water phases were separated completely.

The photo-induced demulsification rate of stable emulsions prepared from SDS/C4AzoTAB mixtures was investigated. Ostwald ripening has been described theoretically by Lifshitz, Slezov, and Wagner (LSW theory) [39, 40]. According to LSW theory, the rate of demulsification based on Ostwald ripening accelerates with increasing interfacial tension between the oil and water phases. Stable O/W-type emulsions consisting of *n*-octane and aqueous SDS/*trans*-C4AzoTAB solutions with  $X_{\text{SDS}} = 0.1$  ( $f_w$ : 0.2) were obtained with a total surfactant concentration greater than 6 mM. The octane and aqueous surfactant solution phases were fully separated from the stable emulsions at total surfactant concentrations of 7 and 10 mM, whereas the emulsions at a total surfactant concentration of 20 mM were not demulsified completely by UV irradiation for 6 h. UV irradiation caused complete phase separation within 60 min with a total surfactant concentration of 7 mM and in 90 min with a total surfactant concentration of 10 mM. The time required for demulsification at 7 mM was shorter than that at 10 mM. The differences in interfacial tension between the *trans* and *cis* isomers at 7 and 10 mM were 16.6 and 10.2 mN m<sup>-1</sup>, respectively, whereas there was almost no difference in interfacial tension between the *trans* and *cis* isomers at 20 mM. Therefore, a change in interfacial tension with UV light irradiation was correlated with the photoinduced demulsification rate. On the macroscale, it takes 90 min for stable emulsions consisting of octane and 10 mM of aqueous SDS/*trans*-C4AzoTAB solution with  $X_{\text{SDS}} = 0.1$  ( $f_w$ : 0.2) to separate completely under UV light irradiation. When the emulsions are placed in vials, UV light illuminates only the surface of the vial, barely penetrating the emulsions because the emulsions are turbid, as shown in Fig. 2.5b. Therefore, UV irradiation will accelerate demulsification if the path length of the emulsions can be reduced. Here, a microreactor was used to reduce the path length of the emulsions. The stable emulsions were pumped through the microreactor using a syringe pump under UV irradiation (Fig. 2.7). When the emulsions flowed through the microreactor at 70 mL h<sup>-1</sup> with UV irradiation, the octane and aqueous surfactant solution phases were separated completely within 3.5 min. The time required for photoinduced demulsification in the microreactor was 26 times shorter than that in a vial. In addition, no phase separation was observed when the microreactor was used in the absence of UV irradiation. Thus, the demulsification in the microreactor was triggered only by UV light.

The homogenization and photoinduced demulsification of mixtures consisting of *n*-octane and 10 mM of an aqueous SDS/C4AzoTAB solution with  $X_{\text{SDS}} = 0.1$  ( $f_w$ : 0.2) were repeated. The emulsions prepared, using a mixture of SDS/*trans*-C4AzoTAB,



**Fig. 2.7** Geometry of the demulsification of stable emulsions in a microreactor. An emulsion consisting of *n*-octane and an aqueous SDS/*trans*-C4AzoTAB solution was pumped through the microreactor using a syringe pump with UV light irradiation. Reprinted with the permission from Ref. [35]. Copyright 2016 American Chemical Society



**Fig. 2.8** Change in the height of the *n*-octane phase separated from stable emulsions consisting of octane and a 10 mM aqueous SDS/*trans*-C4AzoTAB solution with  $X_{\text{SDS}} = 0.1$  ( $f_w$ : 0.2) with repetitive *trans*–*cis* photoisomerization and homogenization. The height of 1.5 cm corresponds to complete phase separation. *Solid lines* photoisomerization with UV light irradiation; *dashed lines* visible light irradiation and homogenization. *Open circles* SDS/*trans*-C4AzoTAB; *filled circles* SDS/*cis*-C4AzoTAB. Reprinted with the permission from Ref. [35]. Copyright 2016 American Chemical Society

were irradiated with UV light. Subsequently, visible light irradiation of the aqueous surfactant solution phase, which had been separated from the emulsions, induced photoisomerization from the *cis* to *trans* isomer. The separated octane and aqueous surfactant solution phases were then homogenized to prepare the emulsions. Thus, the reversible process of homogenization and photoinduced demulsification was observed (Fig. 2.8). Repetitive *trans*–*cis* photoisomerization led to complete phase separation. Therefore, the SDS/C4AzoTAB mixtures can be applied repetitively to the photoinduced demulsification.

In conclusion, stable O/W-type emulsions could be prepared from *n*-octane and aqueous SDS/*trans*-C4AzoTAB solutions, whereas no emulsions were obtained using SDS/*cis*-C4AzoTAB mixtures. UV irradiation led to a change in the emulsification abilities of the SDS/C4AzoTAB mixtures and an increase in interfacial tension between octane and aqueous mixed-surfactant solution. The stable emulsions were demulsified fully by UV irradiation for 90 min, which was shorter than the photo-induced demulsification of stable emulsions prepared using C<sub>7</sub>-azo-C<sub>7</sub> (6 h). The use of a microreactor reduced the time required for the photoinduced demulsification to 3.5 min. This photo-induced demulsification was caused by the Ostwald ripening of octane droplets. Repetitive *trans*–*cis* photoisomerization of the aqueous SDS/C4AzoTAB solutions in the emulsions resulted in photo-induced demulsification. Overall, the photo-induced demulsification demonstrated in this chapter will be useful for industrial applications.

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